SCR Deactivation Mechanisms Related to Alkali and Alkaline Earth Elements

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77 West 200 South, Suite 210
Salt Lake City, Utah 84101

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REI SCR Catalyst Deactivation Program

- DOE- and EPRI-funded program:
  - REI
  - University of Utah (UU)
  - Brigham Young University (BYU)
  - Stan Harding (N.S. Harding Associates)
  - Catalyst manufacturers
- Principal Tasks:
  - Fundamental analysis of SCR catalyst poisoning and regeneration (BYU)
  - Multi-catalyst slipstream reactor to be tested at two utility boilers for six months (REI, UU)
  - SCR deactivation model suitable for CFD code (REI)

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Mechanisms for SCR Catalyst Deactivation

- Fouling (surface deposition)
  - Deposition of ash
  - Sulfation of deposit observed with PRB
- Pore condensation (and/or pore blockage)
- Poisoning
  - Vapor-phase As (as As_2O_6) thought to react with active sites in some cases

Literature suggests fouling plays a role in deactivation from both PRB and biomass

Pore condensation could be a factor

Subtask 1 – Catalyst Deactivation Studies

- Laboratory investigation at BYU using small catalyst samples
- Effects of alkali impurities on reactivity
- Characterization of catalyst (physical and chemical) before and after lab/field testing
  - Adsorption studies in flow reactor
  - Surface analysis (e.g. XPS), TEM/SEM, XRD, FTIR, TPD
  - No chemical analysis of any commercial catalysts.
- *Current Status:* Literature search completed; NO_x activity measurements and spectroscopy of catalysts underway at BYU

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Two Primary Analysis Systems

- *In situ* spectroscopy reactor (ISR)
  - FTIR analyses of SO_2, NH_3, and NO_x adsorption and desorption behaviors:
  - Obtain quantitative Brønsted and Lewis acidities on fresh and exposed surfaces based on spectral signatures
  - Determine surface kinetics and active sites
- Catalyst characterization system (CCS)
  - Obtains quantitative activities/deactivation
  - Focuses on kinetic coefficient and mechanistic information
  - Simulates industrial flows with compositions of: NO, 0.10%; NH_3, 0.1%; SO_2, 0.1%; O_2, 2%; H_2O, 10%; and He, 87.7%
  - Custom and commercial catalysts tested as fresh samples and after exposure under both steady and transient conditions

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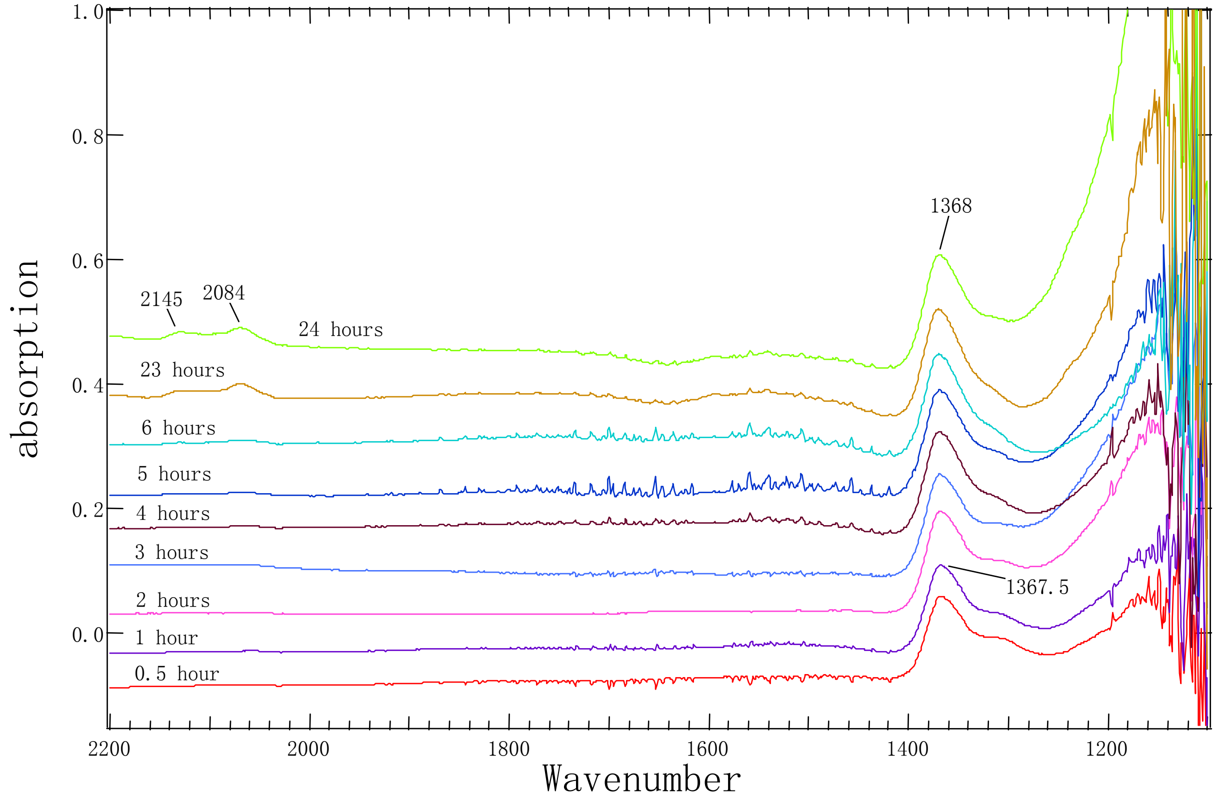
In-situ FTIR Analysis of Catalyst Sulfation

5% V_2O_5/TiO_2 during wet sulfation



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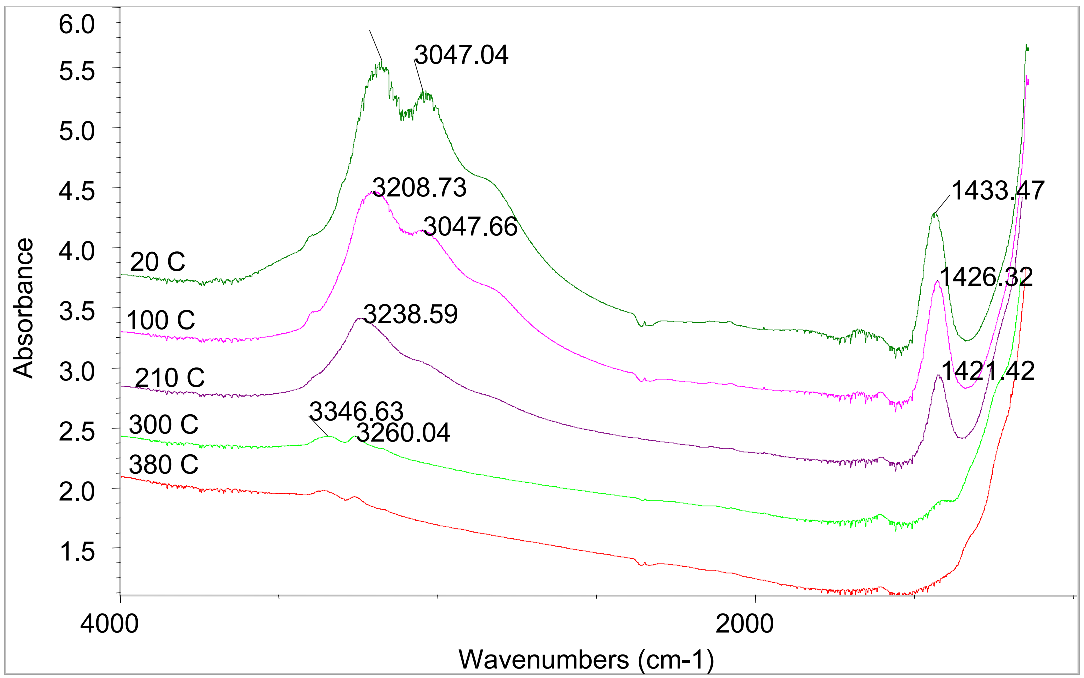
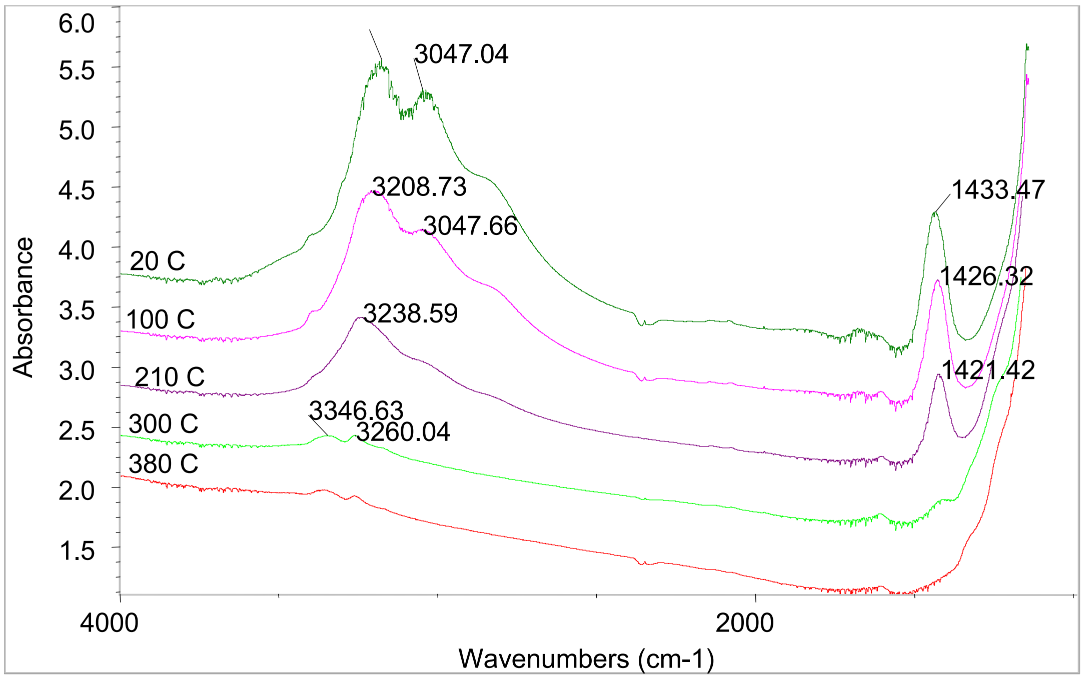
Ammonia Adsorption on Sulfated Catalyst



After exposure to NH_3, three new bands:

- Bending vibration of NH_3 chemisorbed on Brønsted acid sites (1433 cm^{-1})
- Stretching vibration of NH_3 adsorbed on both Brønsted (~ 3030 cm^{-1}) and Lewis acid (~3350 cm^{-1}) sites

Ammonia Adsorption on Sulfated Catalyst



Conclusion:

- Sulfation helps to increase surface acidity, especially Brønsted acidity
- Ammonia adsorbs mainly on Brønsted acid sites on sulfated catalyst surface

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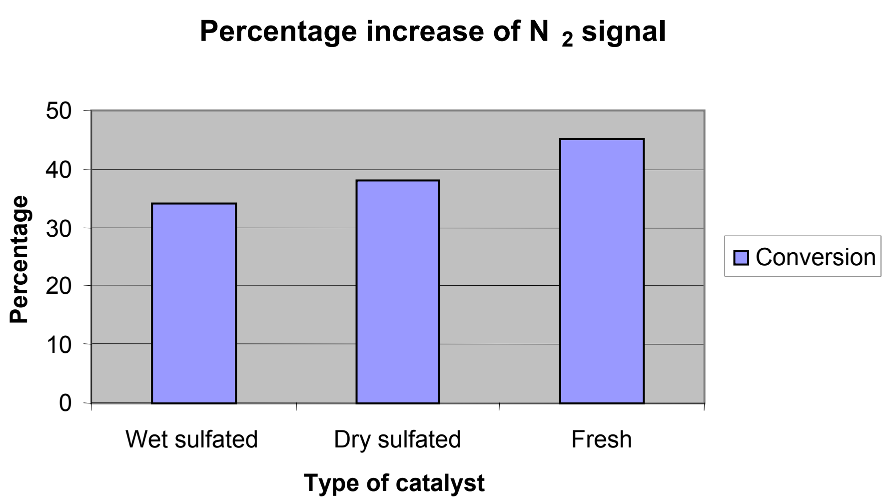
Complimentary Analytical Techniques



- Mass Spectrometry (MS) of products during *in-situ* FTIR
  - Surface reaction of $NO+NH_3$
  - Effect of catalyst pretreatment
- XPS (surface composition analysis) of catalysts exposed at 380°C

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Complimentary Analytical Techniques

	Wet sulfated	Wet Sulfated	Dry sulfated
	Sulfur Atom%		
with NH_3 adsorption	1.87	0.77	0.15
without NH_3 adsorption	0.00	0.00	0.00

- Mass Spectrometry (MS) of products during *in-situ* FTIR
  - Surface reaction of NO+NH_3
  - Effect of catalyst pretreatment
- XPS (surface composition analysis) of catalysts exposed at 380^{o}C
  - NH_3 adsorption removes surface sulfate species

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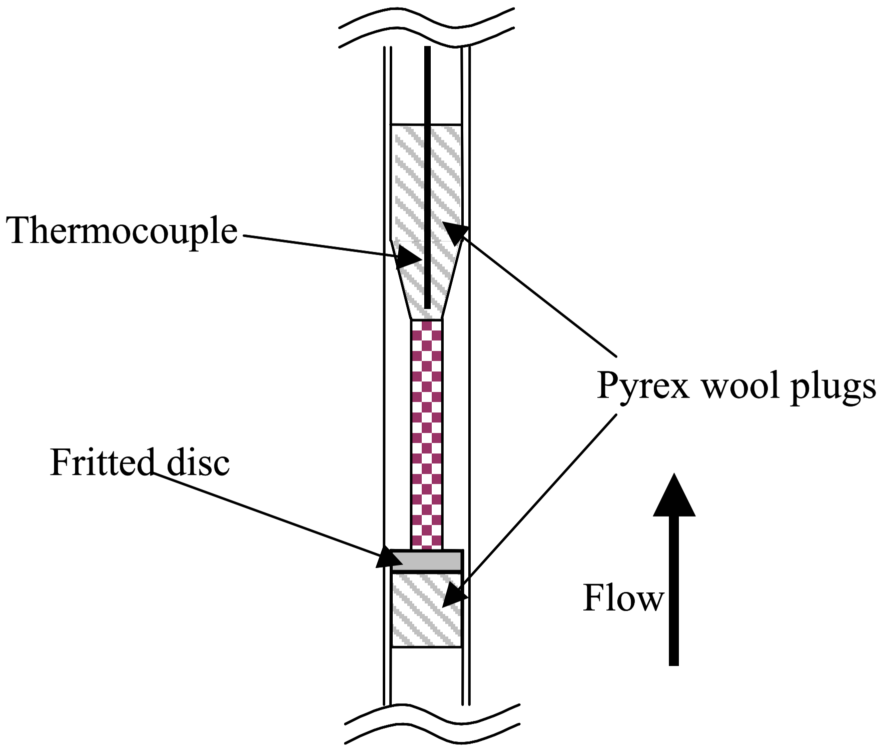
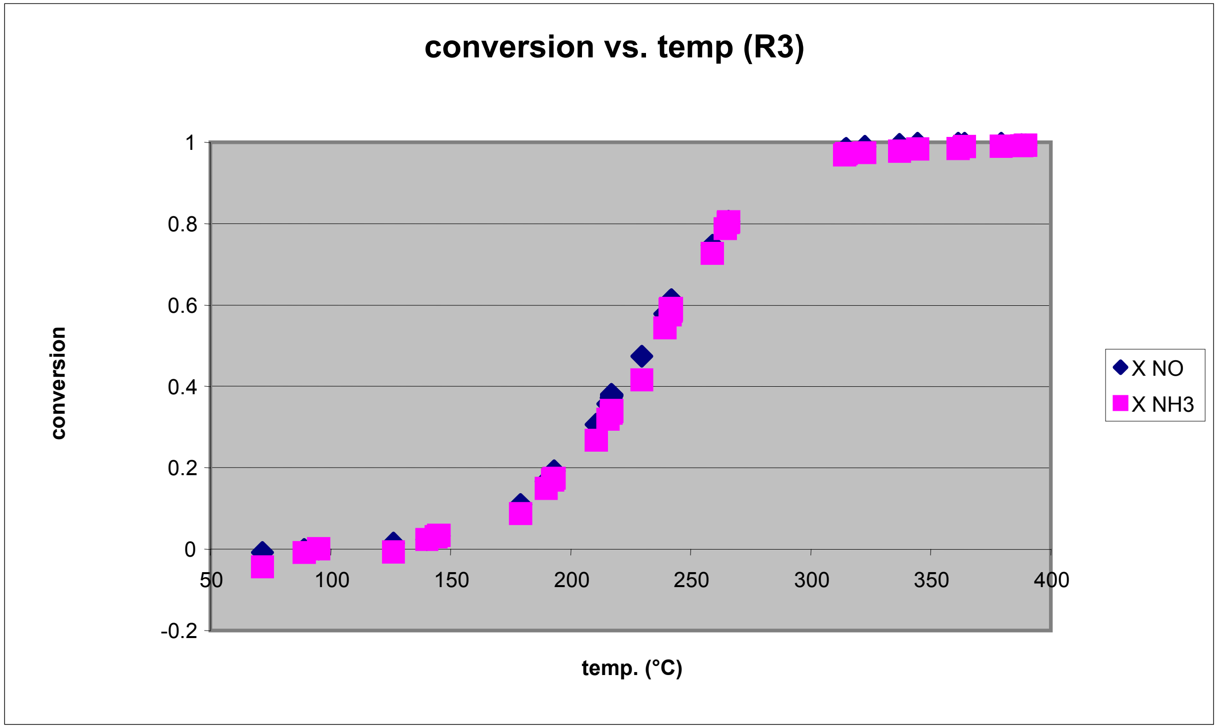
Catalyst Activity Measurement



- Powdered catalyst samples exposed to simulated flue gas:
  - NO, 0.10%; NH_3, 0.1%; SO_2, 0.1%; O_2, 2%; H_2O, 10%; and He, 87.7%
- NO and NH_3 measurements at inlet and outlet
- Four reactors in parallel – multiple catalyst samples evaluated

Catalyst Activity As A Function of Temperature



- Fresh BYU catalyst
- Reactivity (NO conversion) calculated from NO and NH_3 measurements

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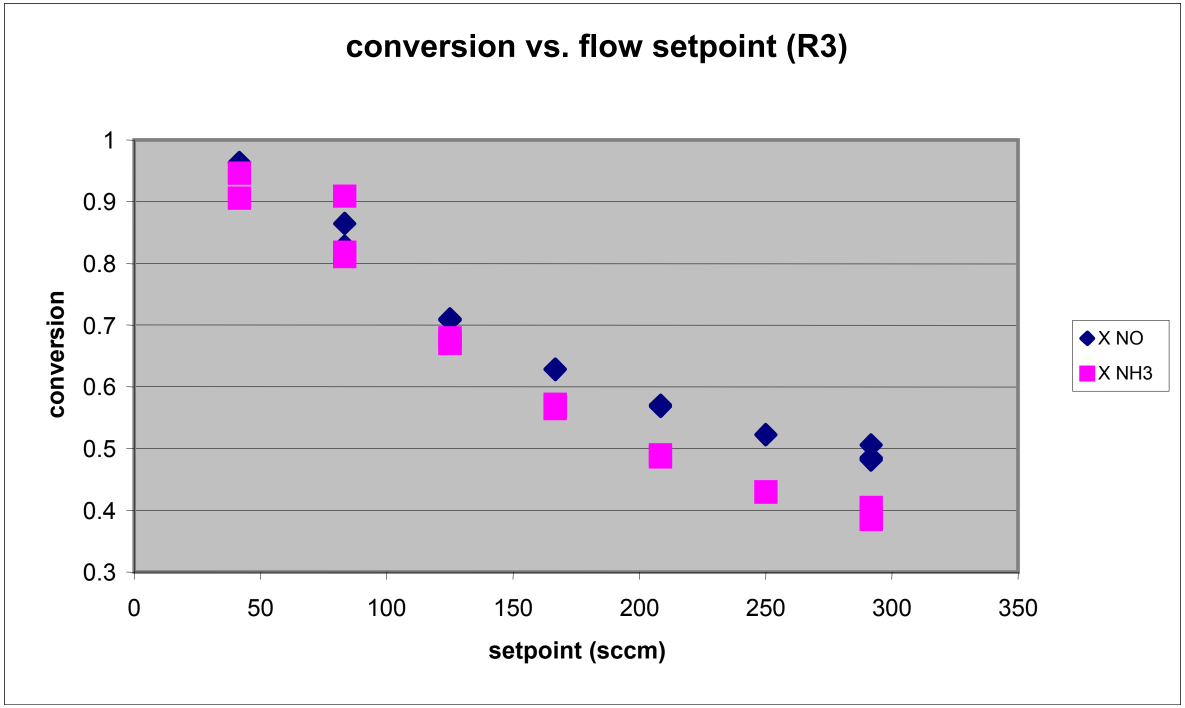
Catalyst Activity As A Function of Space Velocity (Flow Rate)



- Fresh BYU catalyst
- Reactivity (NO conversion) calculated from NO and NH_3 measurements

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Status and Preliminary Conclusions: Lab Studies

- *In-situ* spectroscopy reactor (ISR)
  - Ability to observe adsorption of key species on surface as a function of temperature and gas composition
  - Future work on poisoned and aged catalyst samples
- Catalyst characterization system (CCS)
  - Custom catalysts tested (fresh samples)
  - Future work on poisoned and aged catalyst samples from field testing

Subtask 2 – Field Testing in Slipstream

- Six catalysts evaluated in parallel
  - Four vendors have supplied catalyst; one “generic” catalyst from BYU
- Monitor catalyst activity by
  - NO_x measurement
  - Periodic removal of catalyst samples for lab testing at BYU
- First test: AEP Rockport Unit 1
  - Burns PRB-bituminous blend

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Features of Reactor Design

- Multiple catalysts in parallel (plate and honeycomb)
- Catalyst exposed to gas and particulate matter
- Velocity of full-scale SCR
- 1 ½ - 3 foot catalyst samples to avoid favoring end effects
- On-line, continuous NO_x measurement for detailed kinetic information

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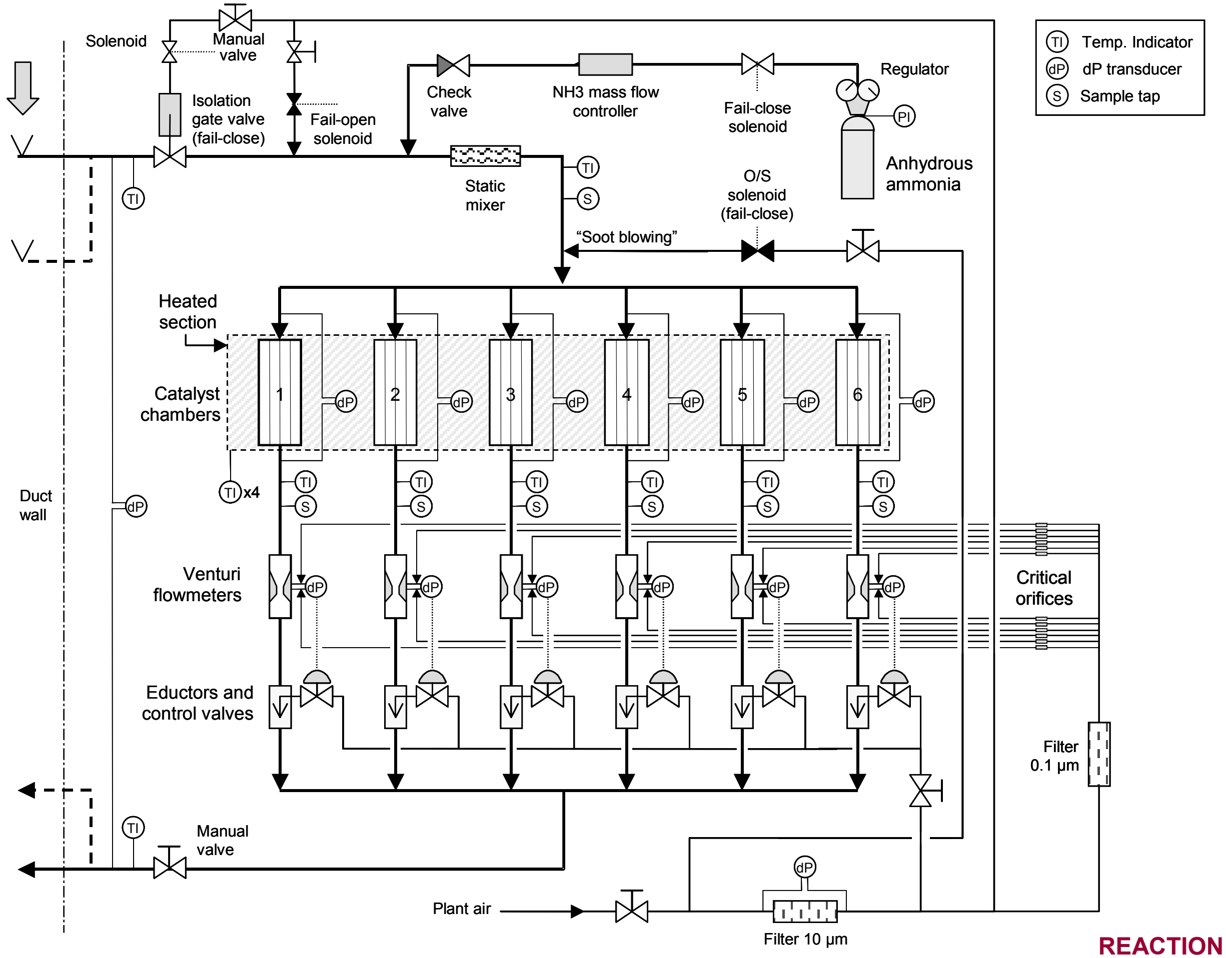
Reactor Schematic



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SCR Reactor
Installation at Rockport Plant

Inlet line being installed

Reactor installed across air preheater

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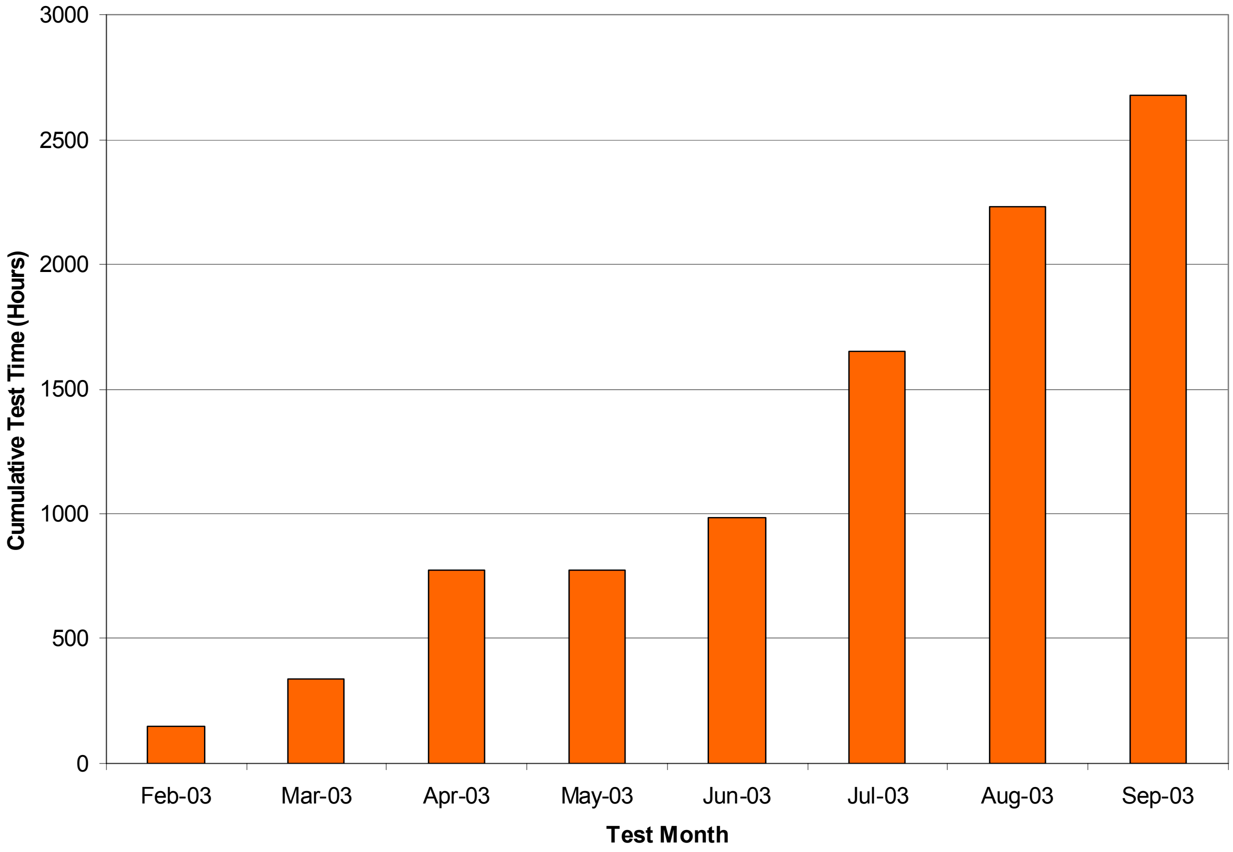
SCR Control System

- Embedded microcontroller
- Ethernet link to local PC for data logging and communication
- Controlled remotely by REI

Operating Experience



~2700 hours of cumulative flue gas exposure

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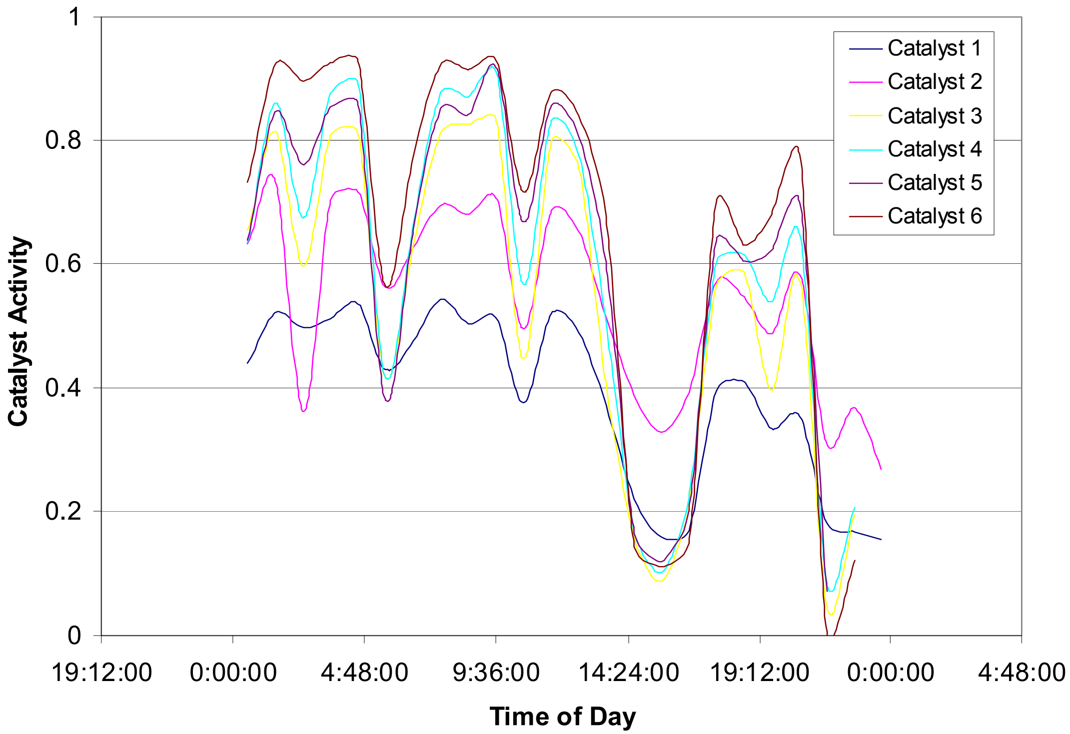
Catalyst Activity



- Activity measured using inlet and outlet NO
- NH_3/NO ratio = 1.1

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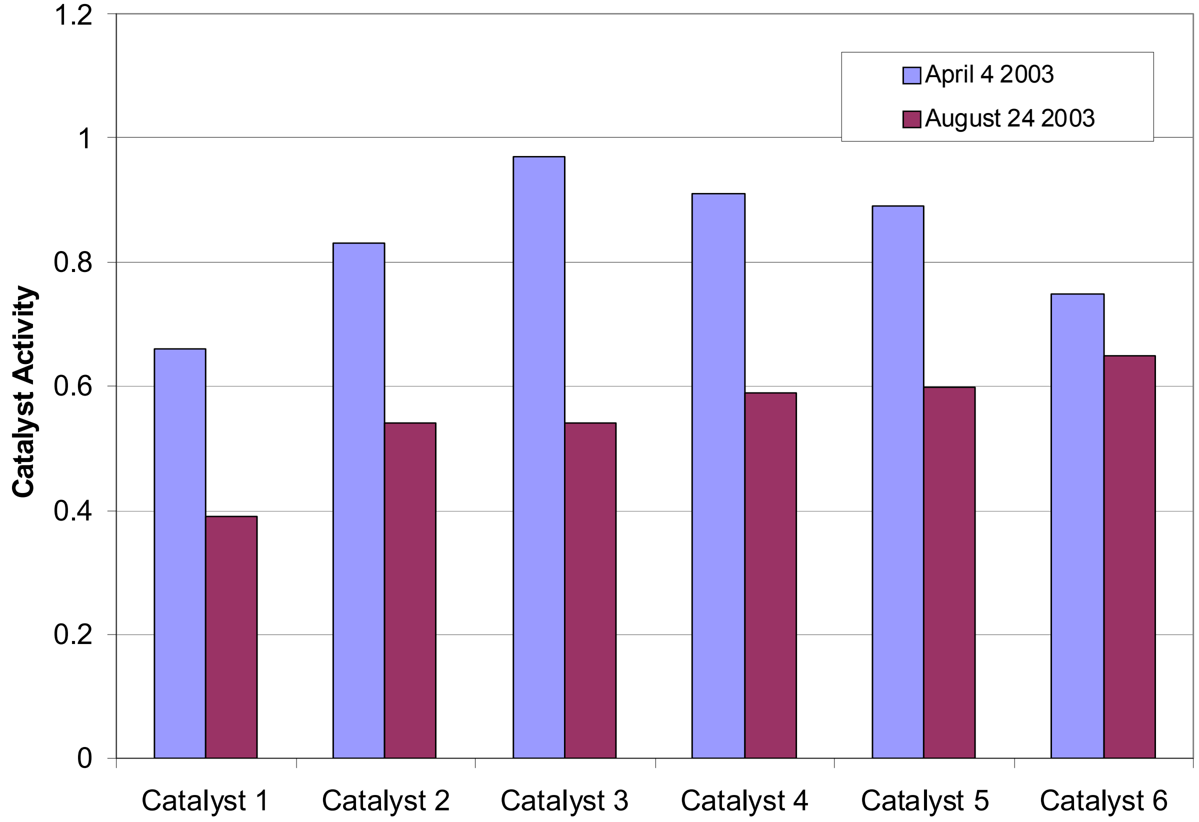
Change in Catalyst Activity: April to August



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Status and Preliminary Conclusions: Slipstream Reactor Studies

- 2700 hours of operating experience
- On-line activity measurements made
- 25% of catalyst samples have been pulled for lab analysis
- Plant is currently in an outage, back in November
- Testing will continue for another 3 months

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Subtask 4 – Deactivation Model

- REI developing SCR reactor model for overall power plant model
- Formulate deactivation sub-model based on laboratory and field testing
- Integrate with REI SCR model

Current Status: Preliminary SCR model implemented

EPRI

BYU

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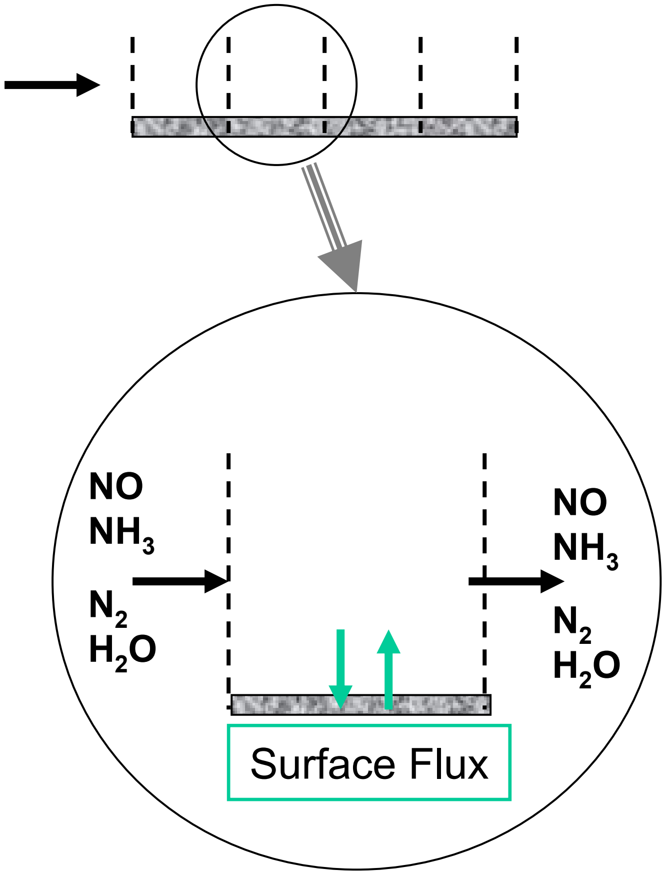
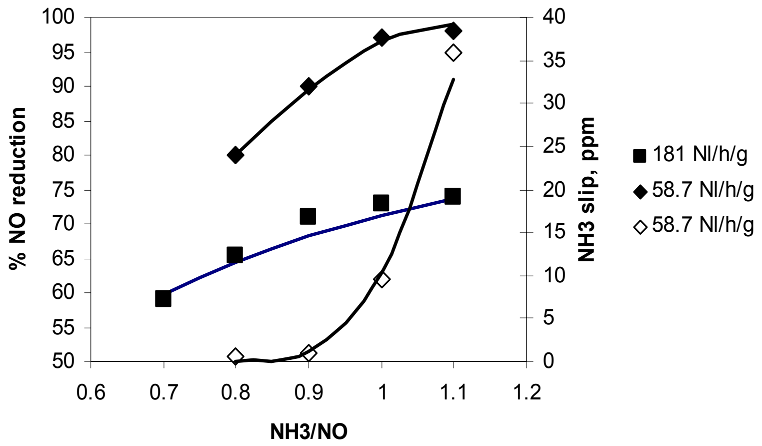
SCR Model – Approach

- Solve gas transport and surface reactions along length of catalyst
- Surface equations are solved
  - Surface species concentrations of specific sites
  - Steady state assumption
  - Solution dependent on local gas species concentration
- Effectiveness factor to compensate for porous diffusion
- Gas species transport equations
  - Rates from surface equation solution



1D Model - Status



NO reduction and NH_3 slip for two space velocities (181 Nl/h/g and 58.7 Nl/h/g). Filled symbols indicate NO reduction and open symbols indicate ammonia slip concentrations.

- 1D model has been validated against open literature data *[Dumesic et al., J.Catal,* ***1996****, 163, 409-417]*
- Model includes effectiveness factor for catalyst pore diffusion
- Catalyst deactivation or poisoning to be added

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